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Title: Towards resolving the Rare Earth Crisis: Acquiring thermodynamic data required for modelling of the formation of Th-bearing monazites

Author(s): Migdisov, Artaches
Nisbet, Haylea Dawn

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Towards resolving the Rare Earth Crisis: Acquiring thermodynamic data required for modelling of the formation of Th-bearing monazites.

Geoscience: Emerging Ideas R&D Project

A.Migdissov and H.Nisbet (EES-14)

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Part 1. Natural transport and fractionation of REE: insights for resolving the REE crisis.

A. Migdisov

Periodic Table of the Elements

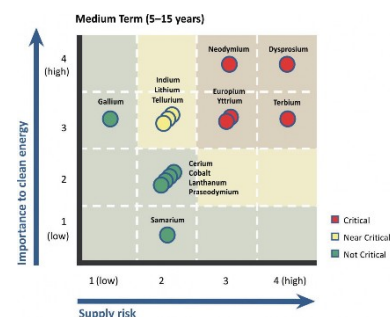
The periodic table shows elements from Hydrogen (H) to Oganesson (Og). The Lanthanide series (La to Lu) and Actinide series (Ac to Lr) are highlighted in red, indicating their relevance to the REE crisis.

China: controls 97% of the global REE market

2006: China enforced quotas for the export of REE

2011: DOE “Critical materials strategy” report released

2013: DOE “Critical materials institute” hub was created based on the Ames Lab (EERE, AM)



2014: USGS Mineral Resources report “The Rare-Earth Elements - Vital to Modern Technologies and Lifestyles”



hybrid vehicles, rechargeable batteries, wind turbines, cell phones, flat screen display panels, compact fluorescent light bulbs, laptop computers, disk drives, catalytic converters

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Sources of the crisis



- Mountain Pass, California : 16.7 million tons at 7.98 wt% REO
- Bear Lodge, Wyoming: 24.2 million tons at 2.74 wt% REO
- Strange Lake, Labrador–Québec, Canada: 57 million tons at 0.92 wt% REO
- Nechalacho (Thor lake), Northwest Territories, Canada, 110 million tons at 1.59 wt% REO

IEFA Rare Earth Providing qua

LIGHT RARE EARTH METALS		Last Price		Units
Lanthanum metal ≥ 99%	0.0	7.00		US\$/kg
Lanthanum Oxide ≥ 99.5%	0.0	2.00		US\$/kg
Cerium metal ≥ 99%	0.0	7.00		US\$/kg
Cerium Oxide ≥ 99.5%	0.0	2.00		US\$/kg
Praseodymium metal ≥ 99%	0.0	85.00		US\$/kg
Praseodymium Oxide ≥ 99.5%	0.0	52.00		US\$/kg
Neodymium metal ≥ 99.5%	0.0	60.00		US\$/kg
Neodymium Oxide ≥ 99.5%	0.0	42.00		US\$/kg
Samarium metal ≥ 99.9%	0.0	7.00		US\$/kg
HEAVY RARE EARTH METALS		Last Price		Units
Europium Oxide ≥ 99.99%	0.0	150.00		US\$/kg
Gadolinium metal 99.9%	0.0	55.00		US\$/kg
Gadolinium Oxide ≥ 99.5%	0.0	32.00		US\$/kg
Terbium metal ≥ 99.9%	0.0	550.00		US\$/kg
Terbium Oxide ≥ 99.5%	0.0	400.00		US\$/kg
Dysprosium metal ≥ 99%	0.0	350.00		US\$/kg
Dysprosium Oxide ≥ 99.5%	0.0	230.00		US\$/kg
Erbium metal ≥ 99.9%	0.0	95.00		US\$/kg
Erbium Oxide ≥ 99.5%	0.0	34.00		US\$/kg
Yttrium metal ≥ 99.9%	0.0	35.00		US\$/kg
Yttrium Oxide ≥ 99.99%	0.0	6.00		US\$/kg
Scandium metal 99.9%	0.0	15,000.00		US\$/kg
Scandium Oxide ≥ 99.95%	0.0	4,200.00		US\$/kg
Mischmetal ≥ 99%	0.0	6.00		US\$/kg

Hydrochloric Acid, Technical: \$77.00 / 2.5 l
 Sodium hydroxide, Technical: \$43.34/ 5 l
 Sulfuric Acid, Technical: \$92.04/ 2.5 l

	Xenotime (wt%)	Monazite (wt%)
La ₂ O ₃	-	15.29
Ce ₂ O ₃	-	31.21
Pr ₂ O ₃	-	3.57
Nd ₂ O ₃	0.17	8.84
Sm ₂ O ₃	0.49	2.02
Eu ₂ O ₃	0.04	0.01
Gd ₂ O ₃	1.89	0.05
Tb ₂ O ₃	0.6	-
Dy ₂ O ₃	5.15	-
Ho ₂ O ₃	1.06	-
Er ₂ O ₃	3.86	-
Tm ₂ O ₃	0.7	-
Yb ₂ O ₃	4.1	0.35
Lu ₂ O ₃	0.52	-
Y ₂ O ₃	46.49	-
ThO ₂	0.38	1.65
UO ₂	0.96	0.36

Significant radioactive waste stream, requires additional investments

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Potential way toward resolving the crisis:

- **LREE, HREE, U, and Th occur together, but are getting separated in natural ore-forming processes**
- **Nature does not use expensive reagents to do it – temperature only : separation of LREE, HREE, U, and Th occurs during hydrothermal alteration of REE-bearing rocks.**
- **Understanding of the mechanisms responsible for this separation will permit:**
 - To locate new ore bodies (or parts of known ore bodies), which are Th,U – depleted and HREE enriched

Mining only the REE that we need

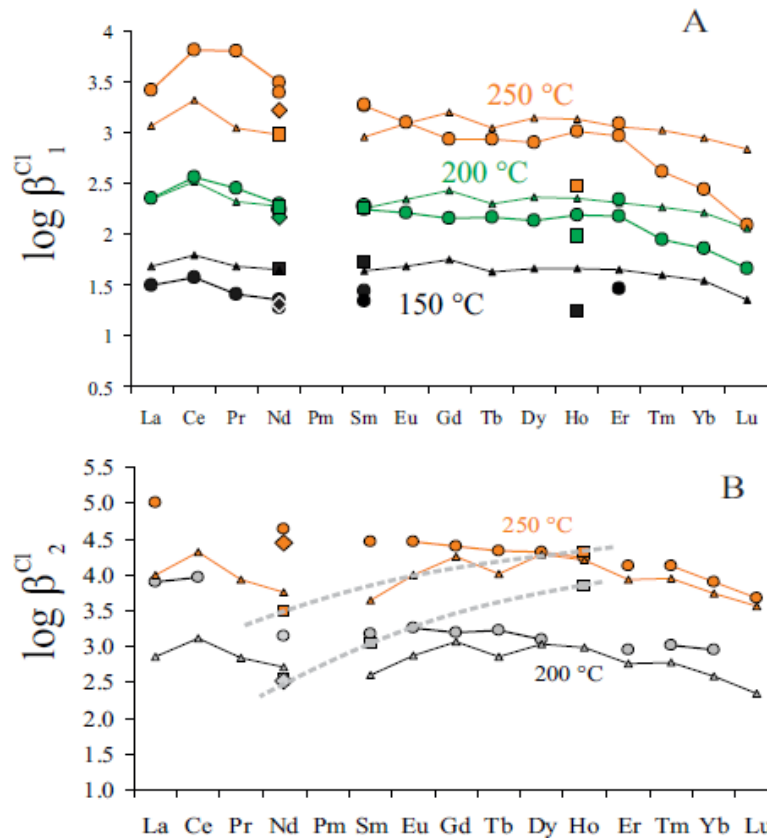
- To develop hydrothermal-based post-mining treatment of ore, which will selectively extract HREE, without mobilizing cheap LREE and radioactive U and Th

Extracting only the REE that we need

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Existing thermodynamic models of ore formation: stability of chloride complexes

NaCl – the main component of solutions from which REE ores have been formed (10 to 40 wt%)



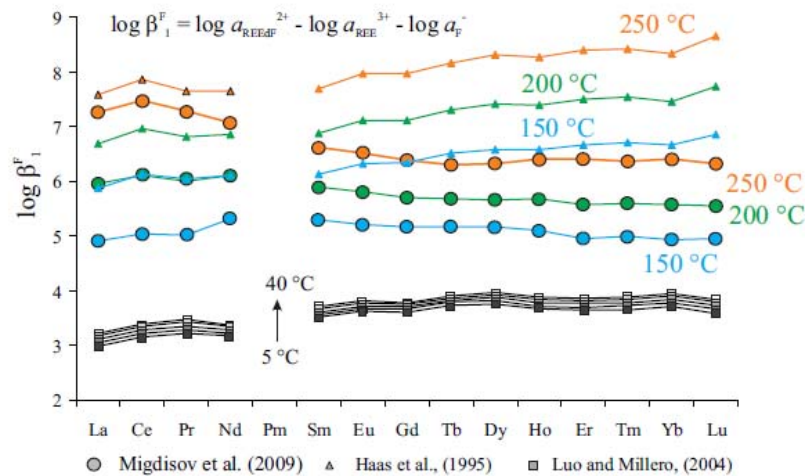
Stability of aqueous chloride complexes of REE (along the REE group):

- Very similar at ambient temperatures
- At elevated temperatures LREE are much more mobile than HREE in Cl-bearing solutions

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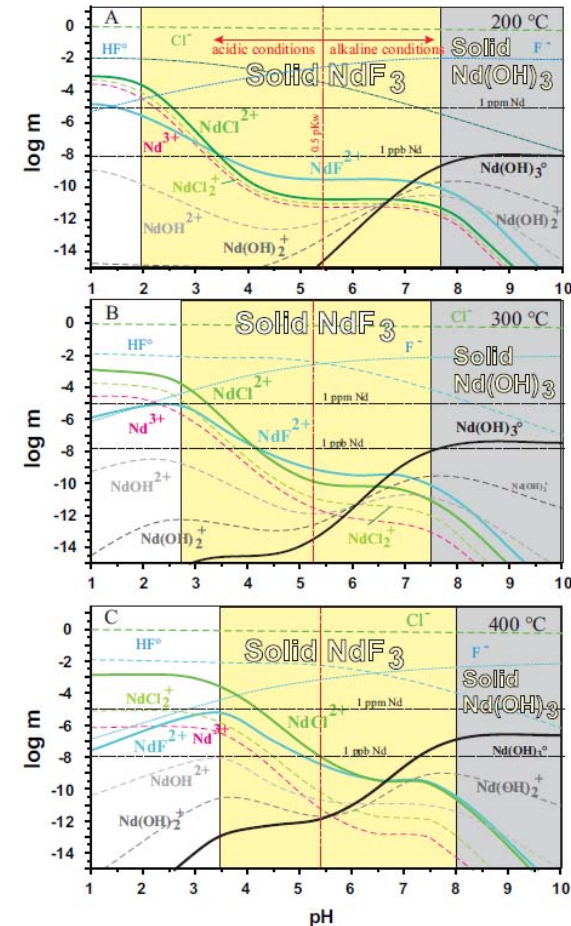
Existing thermodynamic models: stability of fluoride complexes

fluoride – typical for ore-forming solutions (up to thousands of ppm)



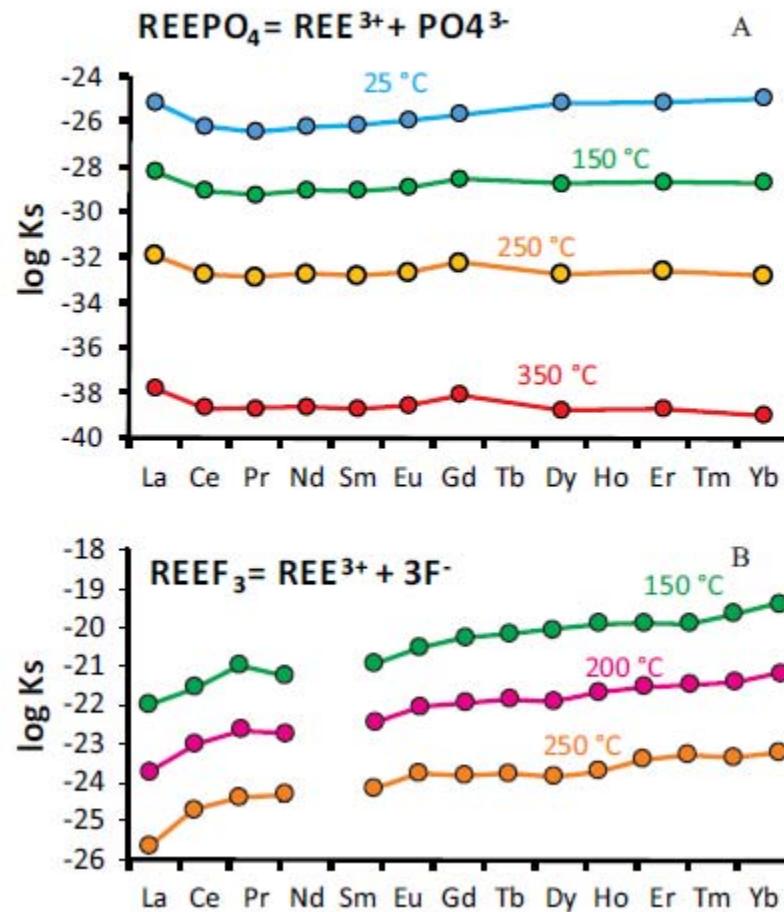
Similarly to chloride species, at elevated T fluoride complexes of LREE are much more stable than these of HREE

However, extremely low solubility of solid REE fluorides precludes anyhow significant transport of REE in F-bearing solutions



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Existing thermodynamic models: properties of solid phases



Solubility of main ore-forming minerals:

- Solubility of phosphate end-members (monazite and xenotime) does not change with atomic number independently of temperature
- Solubility of fluorides (fluocerite) is significantly higher for HREE than for LREE (independently on T)
- Solubility of fluorocarbonates (bastnaesite) – no data available

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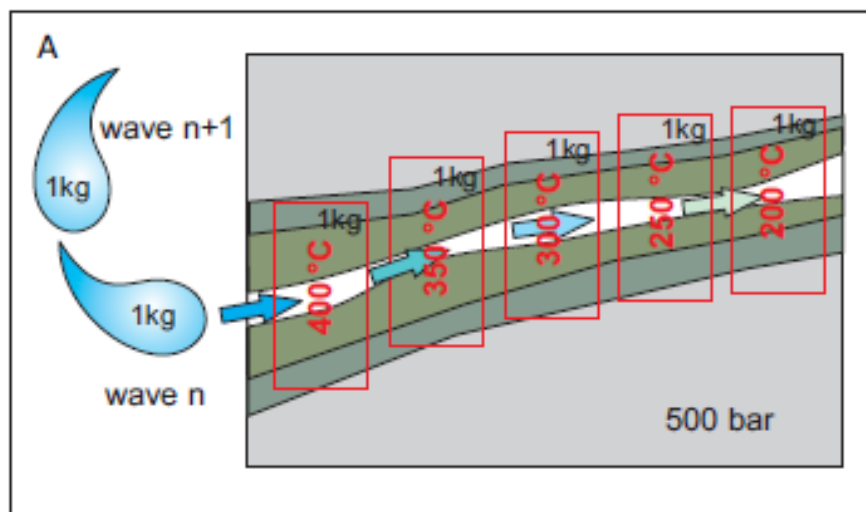
Existing thermodynamic models: separation of REE in natural processes

In acidic solutions (no data is available for non-acidic carbonate-bearing solutions) REE can fractionate:

- In course of mobilization (dissolution) of REE due to differences in mobility of HREE and LREE at elevated T in Cl-bearing aqueous solutions
- In course of deposition of REE from aqueous solution, if deposition occurs in the form of fluorides - due to differences in the solubilities of HREEF_3 and LREEF_3 .

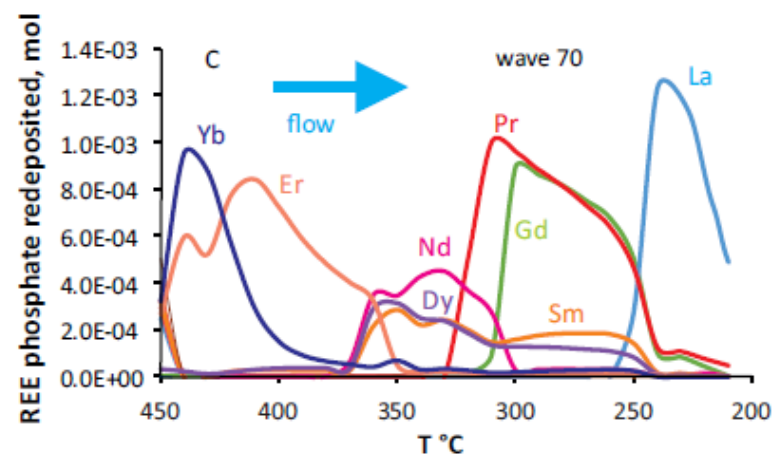
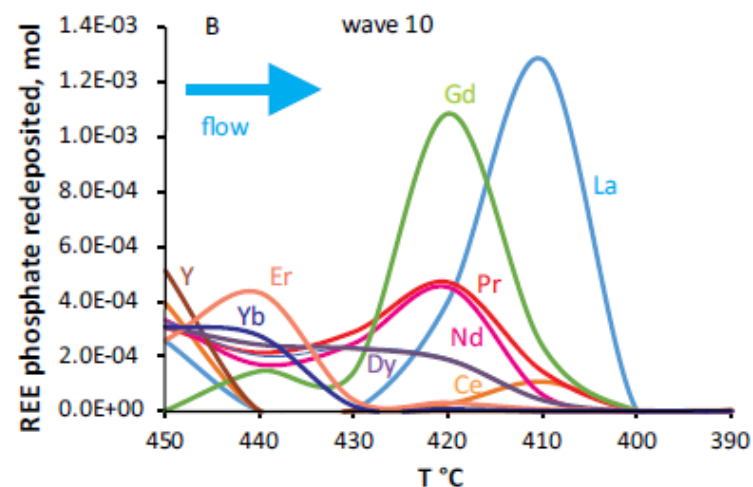
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Existing thermodynamic models: separation of REE in natural processes



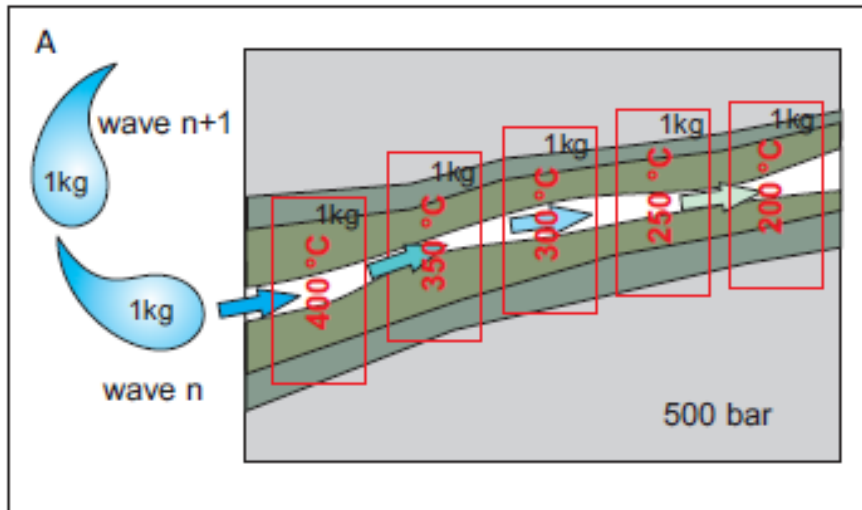
Starting conditions:

- Fluid – 10 wt% NaCl, pH=2.5, 100 ppm of each of the REE
- Rock – chemically inert rock containing 3 wt% of Ca-phosphate (apatite)



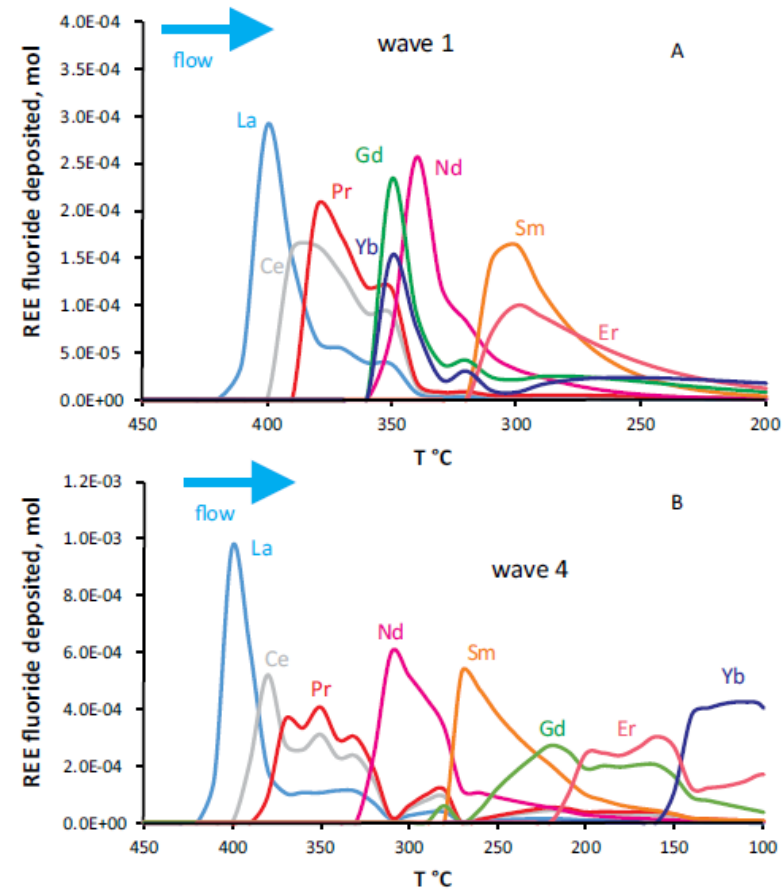
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Existing thermodynamic models: separation of REE in natural processes



Starting conditions:

- Fluid – 10 wt% NaSO₄, pH=2.5, 100 ppm of each of the REE
- Rock – chemically inert rock containing 3 wt% of Ca-fluoride (fluorite)



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Existing thermodynamic models: conclusions

We understand how REE can be separated in acidic Cl-bearing hydrothermal solutions. However,

- No data is available on the behavior of Th and U in such systems – experimental data need to be collected for the stability of Cl, OH, and F aqueous complexes of these metals, and on the stability/solubility of Th-U-REE-bearing solid phases
- No data is available on the behavior of U, Th, and REE in carbonate-bearing systems at elevated temperatures
 - **Crucial! – Large proportion of REE-bearing systems are associated with carbonates**

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Emerging Ideas CSES R&D Project

The ultimate goal of this project is to expand the model currently available for the processes controlling hydrothermal separation of LREE from HREE to REE-Th-bearing and REE-U-bearing systems

Project team:

➤ LANL:

- **Migdissov** – *experimental determination of thermodynamic properties of aqueous species at high T,P (solubility autoclave experiments, spectroscopy)*
- **Xu** – *experimental determination of thermodynamic properties of solids and solid solutions (calorimetry, spectroscopy)*

➤ McGill University, Canada:

- **van Hinsberg** – *experimental determination of trace-level incorporation of elements in mineral structure (solid-melt experiments, solubility experiments)*
- **Williams-Jones** – *natural resources, ore-forming REE-bearing systems (field studies, solubility experiments)*

➤ Student:

- **Nisbet** – post-bac student, will start MSc at McGill in January 2018 with van Hinsberg and Williams-Jones, works at LANL since May 2017

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Emerging Ideas CSES R&D Project

Objectives at the current stage:

- To develop experimental technique and to determine thermodynamic stability of Th-bearing aqueous species in hydrothermal solutions responsible for transport and separation of REE in natural systems (chloride, hydroxyl; sulfate – to be continued with LDRD-DR) (*LANL: Migdissov, Nisbet*)
- To develop the technique of synthesis of Th-bearing monazites for determination of its thermodynamic properties at the following stages of the project (*LANL: Xu, Guo, Nisbet*)

Objectives at the following stages of the project (LDRD-DR):

- To determine thermodynamic properties of Th-bearing monazite solid solutions for a wide range of Th concentrations (from wt% to ppm's level) by solubility and calorimetry techniques (*LANL: high Th monazites: Migdissov, Xu, Guo, Nisbet; McGill: Low Th monazites van Hinsberg, Williams-Jones, Nisbet*)
- To expand the earlier developed thermodynamic model to REE-Th-bearing systems and to prove this model by case studies at natural objects (*Migdissov, Xu, Guo, van Hinsberg, Williams-Jones, Nisbet*)

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Part 2. Experimental determination of thermodynamic properties of Thorium

H. Nisbet

Project Significance:

- Ultimately, our goal is to incorporate Th into models already developed for rare earths
- In order to do this, we need to understand how thorium behaves **in aqueous solution at elevated temperature**

The main goal of my current project is to determine thermodynamic properties of thorium species in Cl-bearing solutions at elevated temperatures

Thorium and Chloride? Counterintuitive?

Th is known to not complex with Cl at low Temperature

- Cl is an important ligand in REE ore-forming hydrothermal systems (up to 40 wt.%)
- U^{4+} was recently found to complex with Cl at temperatures above 200°C

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Previous Studies

- At **ambient temperature**, Th doesn't have any affinity to **chloride**
- In contrast to chloride, thorium has a lot of affinity to **hydroxyl**
 - Moreover, it is known to form **polynuclear** complexes with hydroxyl
 - Whether these polynuclear species **predominate** is under debate
 - We have reason to believe polynuclear species are **de-stabilized at high temperature** (Seward et al, 2014) (though we can not prove it)

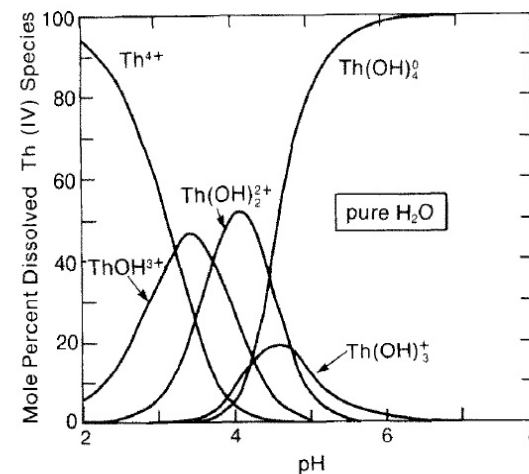
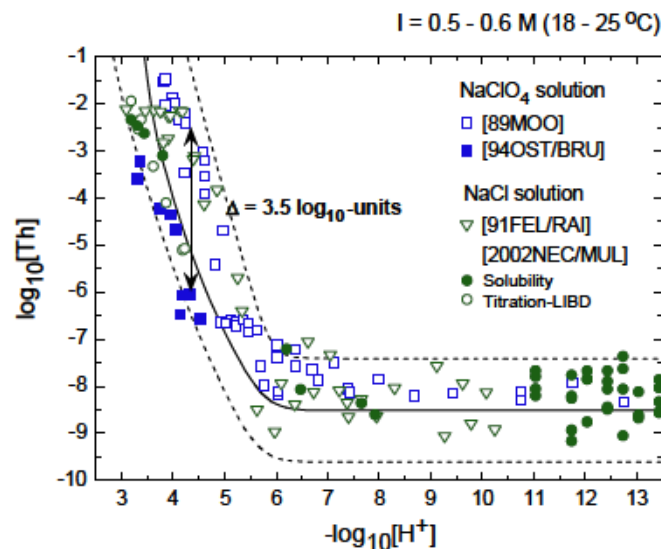


Fig. 3. Distribution of thorium-hydroxy complexes vs pH at 25°C with $\Sigma\text{Th} = 0.01$ ppb in pure water.

Langmuir, D. (1980)

OECD, NEA (2008)

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Immediate Goals

The main goal: to determine thermodynamic properties of thorium species in Cl-bearing solutions at *elevated temperatures*

How?

- By the autoclave solubility method

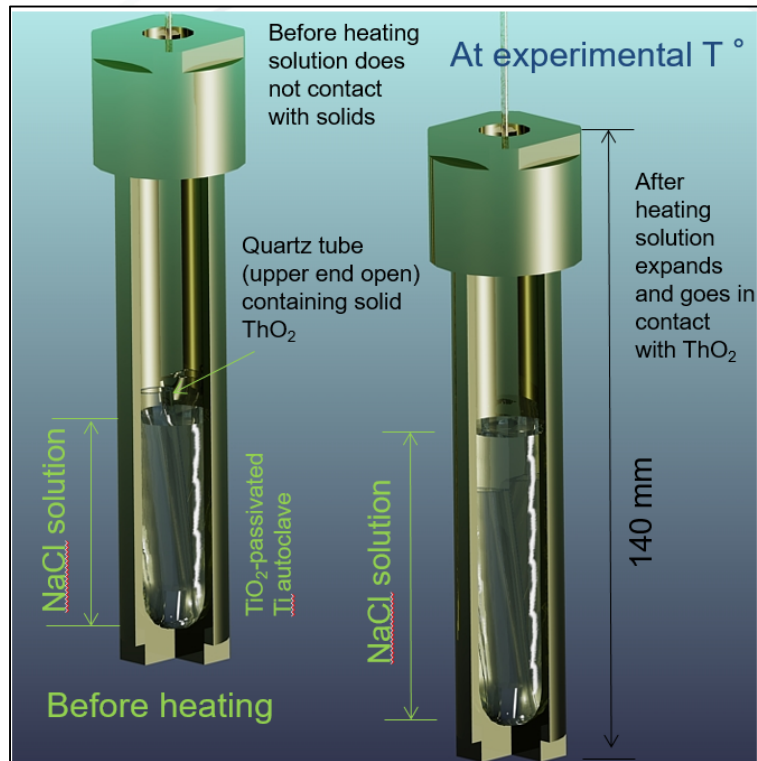
At what conditions?

- Initially, at 25-250°C
- Saturated Water Pressure (SWP)
- Later, higher T and P

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Method

Autoclave Solubility Experiments



Temperatures:
150, 175, 200, 225, 250°C

Pressure:
SWP

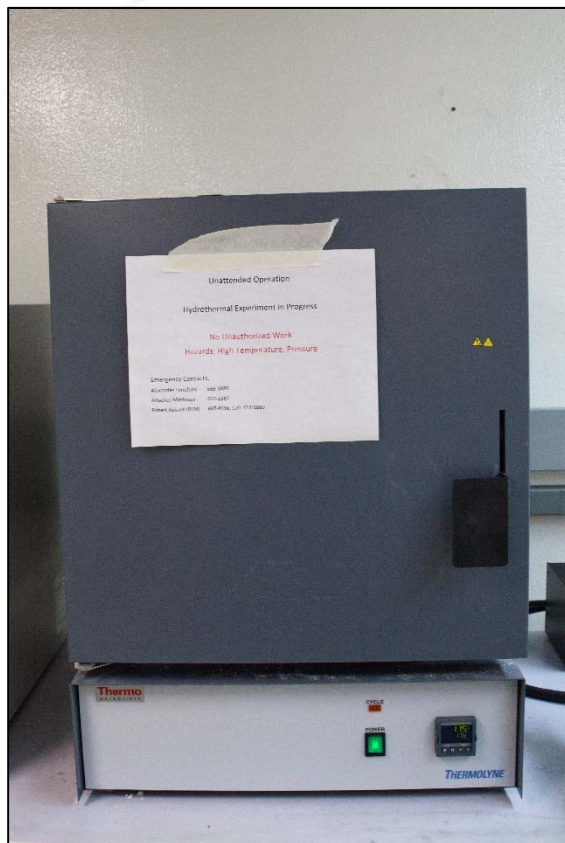
Solutions:
0.25 to 3.5 M NaCl
pH(25°C) 1.5 to 3.5 (HCl)

Reference Solid:
ThO₂

Equipment:
Titanium autoclaves
Teflon reactors w/
stopper
Quartz tubes w/ ThO₂

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Method

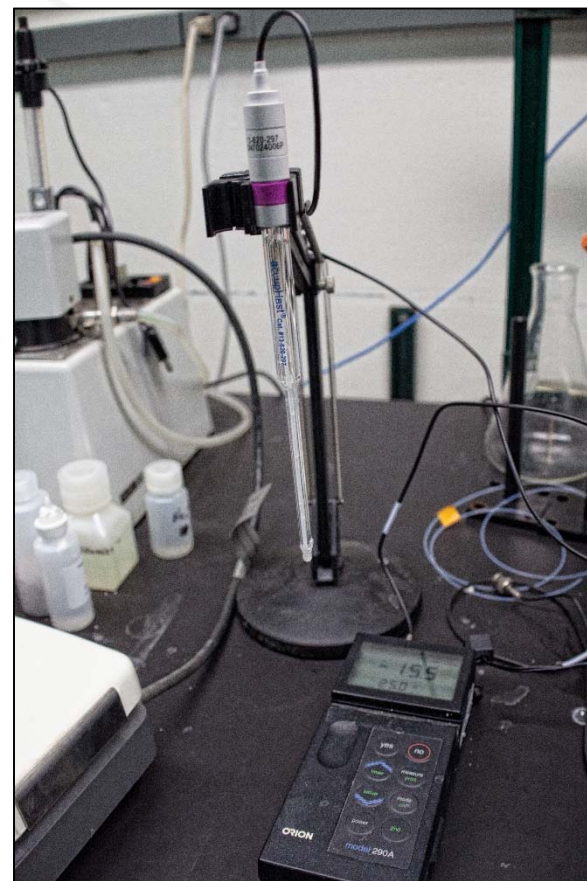


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Method

Calibrations and Calculations

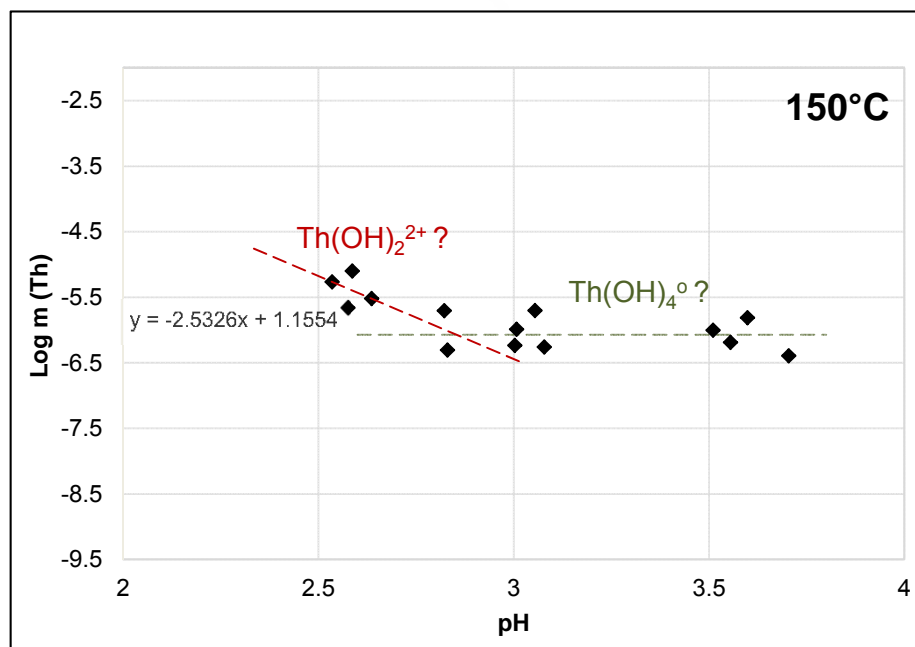
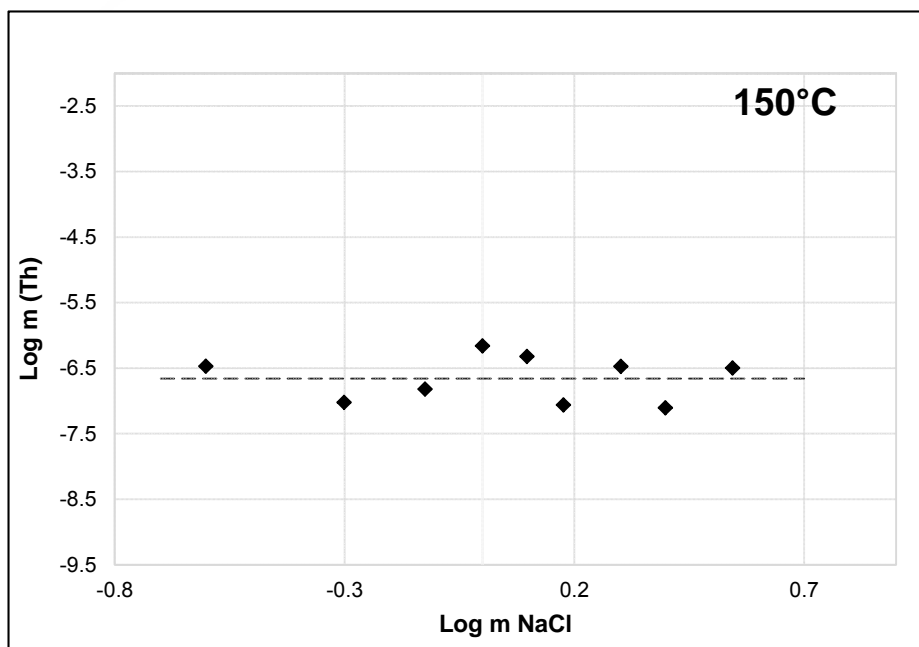
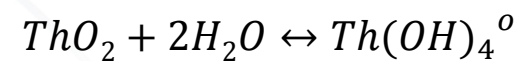
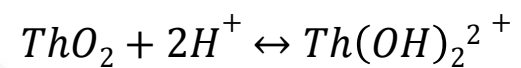
- Measured pH using calibrated pH electrode
- Added 1ml of sulfuric acid to solutions in order to remove possible precipitation that may have occurred during quenching
- Samples analyzed by **ICP-MS** at the Geochemical and Geomaterials Research Laboratory (GGRL) at LANL



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Preliminary results

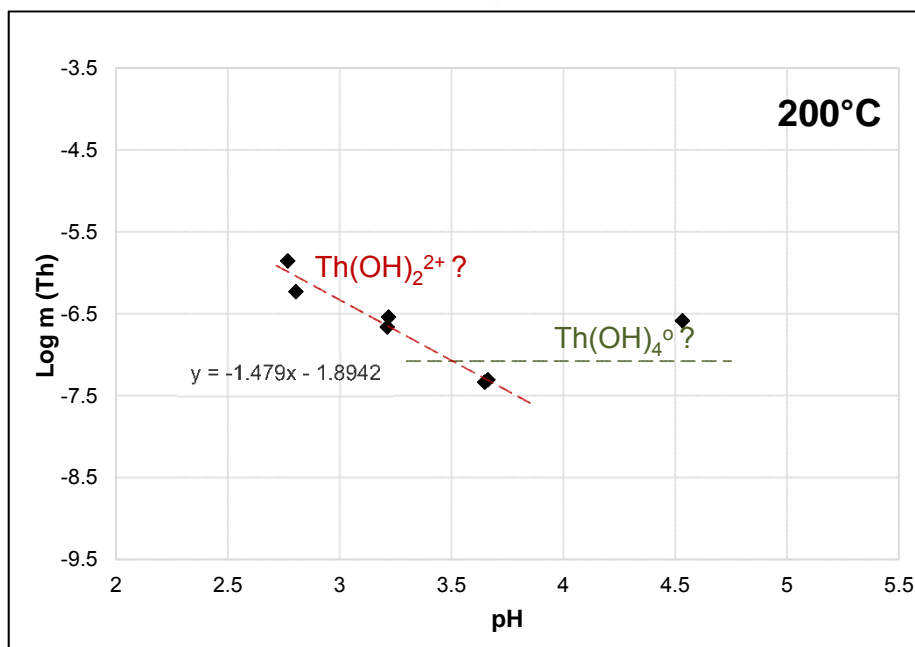
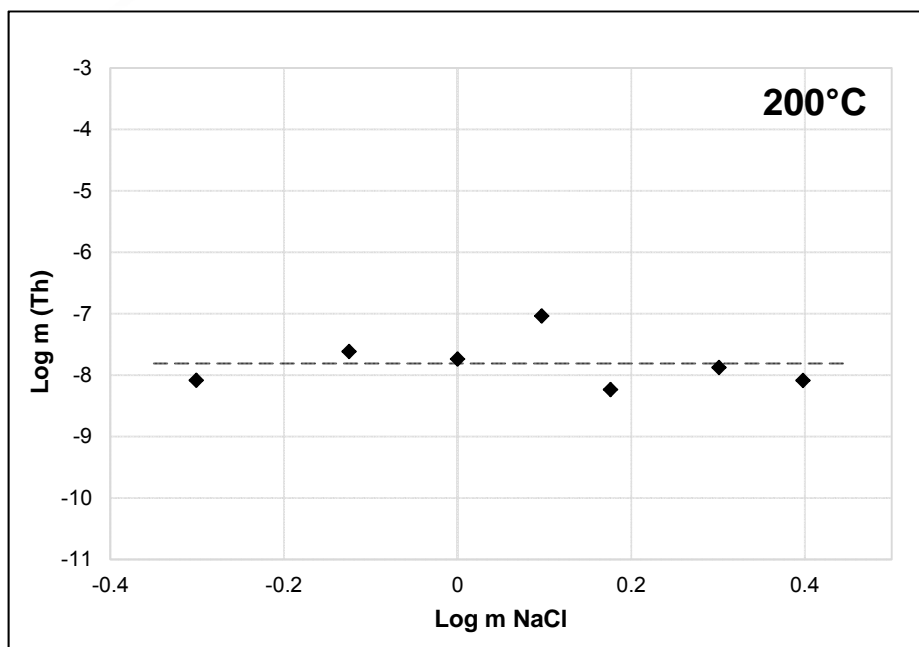
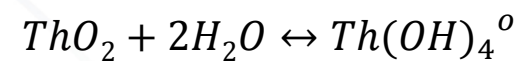
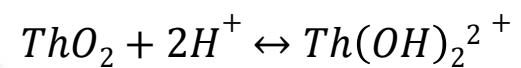
150°C



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Preliminary results

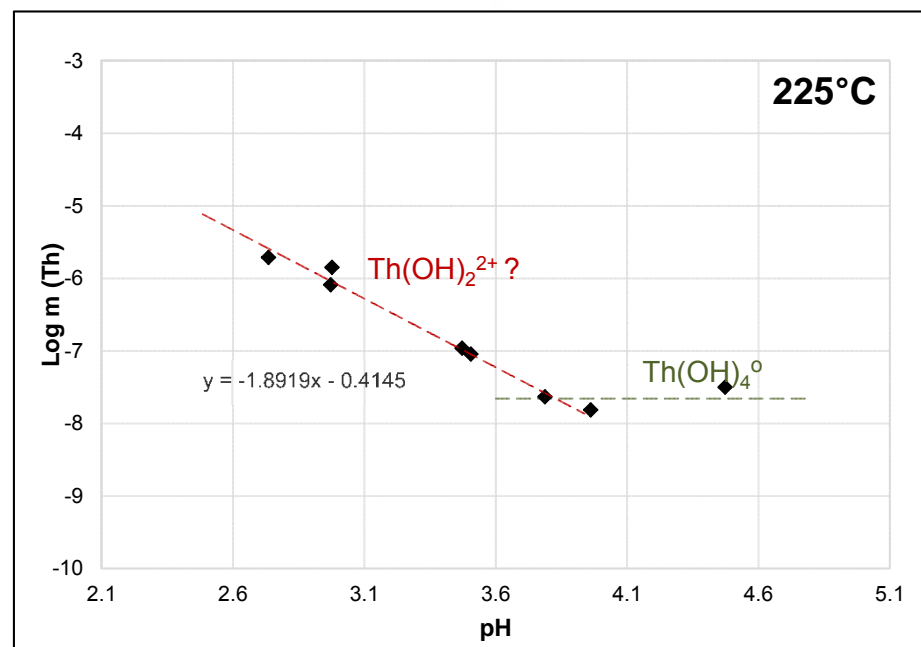
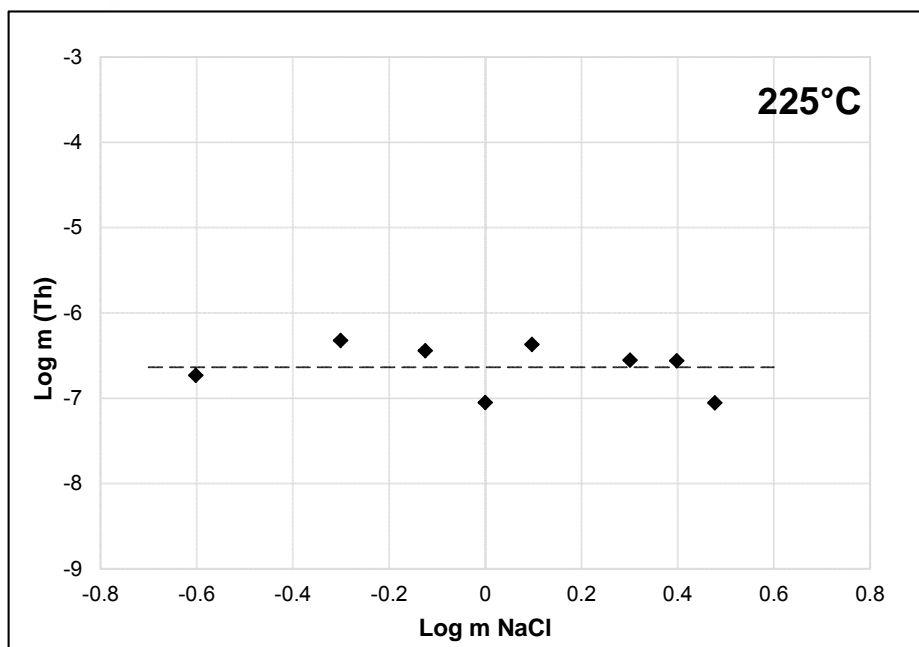
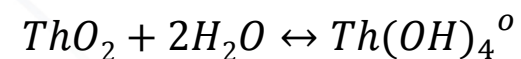
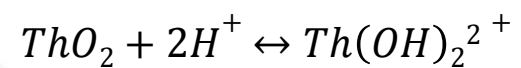
200°C



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Preliminary results

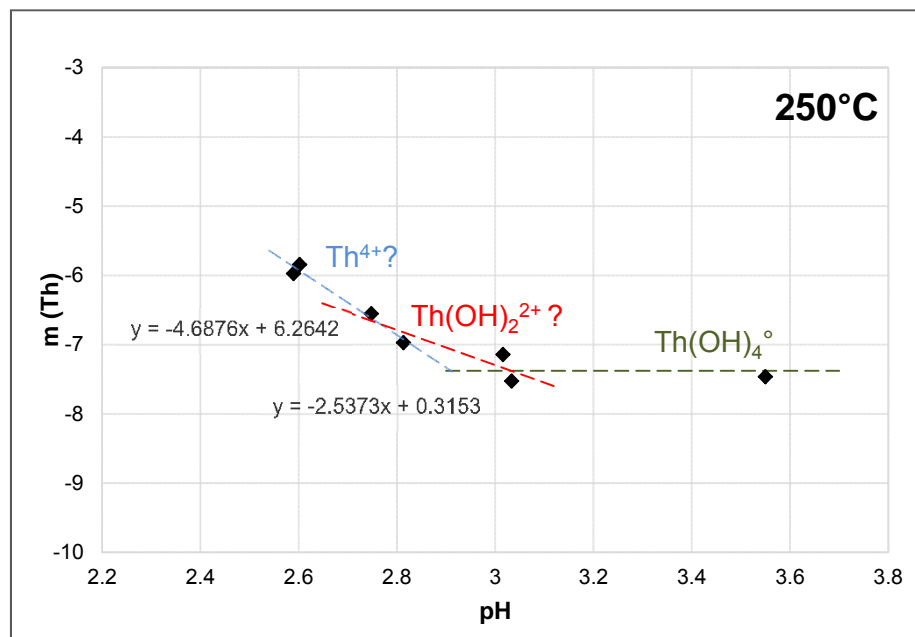
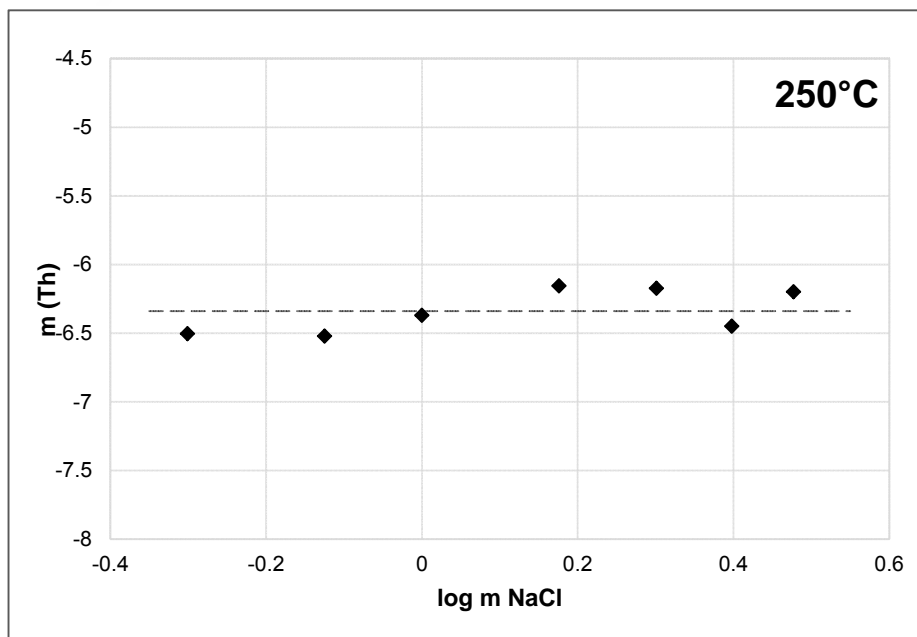
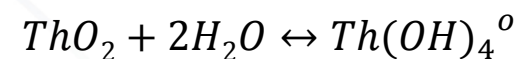
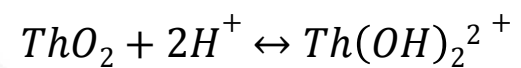
225°C



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Preliminary results

250°C



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Comparing with previous studies

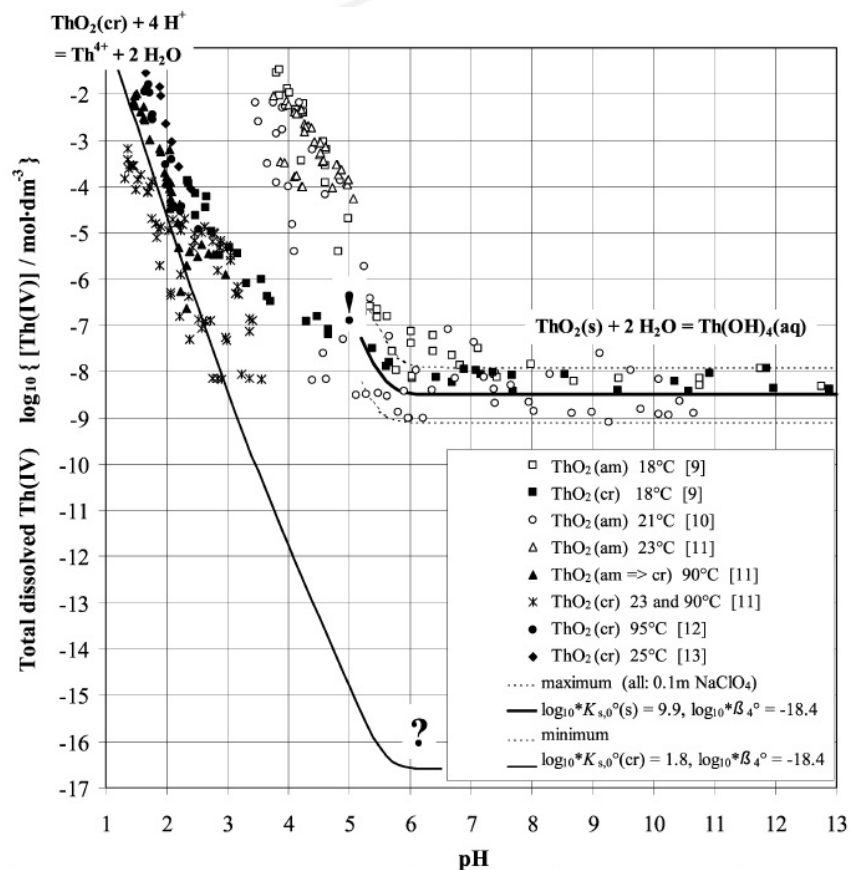
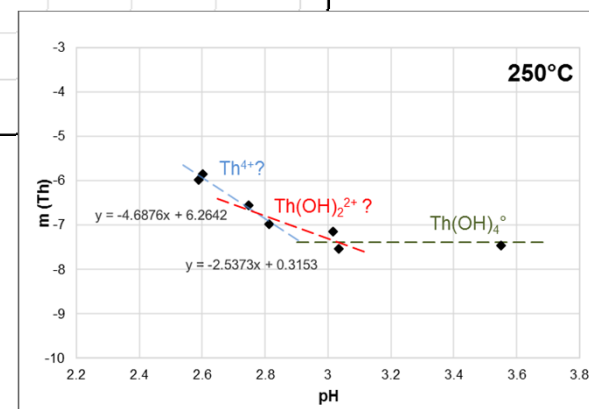
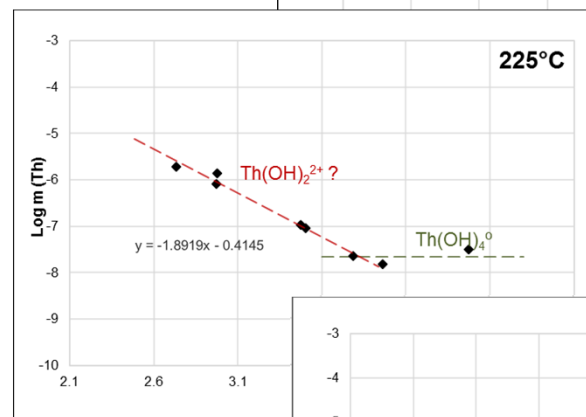
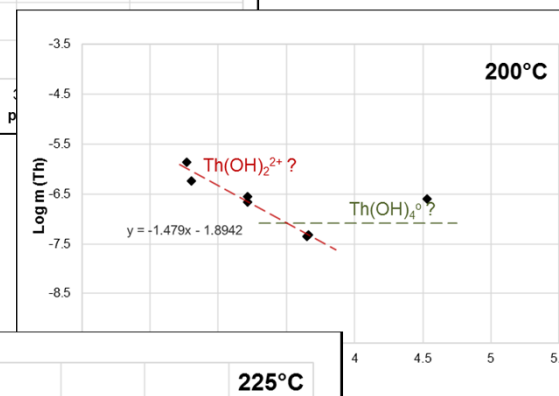
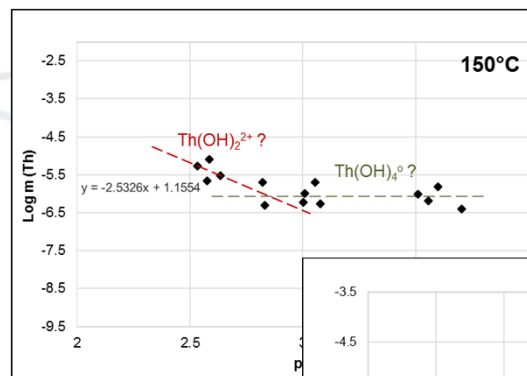


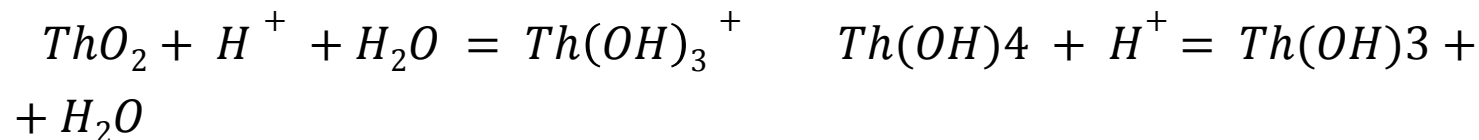
Fig. 2 The enigma of ThO_2 solubility: Data derived from the solubility of crystalline ThO_2 at low pH cannot describe $\text{ThO}_2(\text{s})$ solubility above pH 6 when using independent $\text{Th}(\text{OH})_4(\text{aq})$ formation data (question mark). Vice versa, measured solubilities in alkaline solutions do not point back to the behavior of $\text{ThO}_2(\text{cr})$ at acidic conditions (exclamation mark).



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Preliminary Data Analysis

- No dependence on NaCl concentrations was observed
- Solubility of Th oxide determined in our experiments is 1 to 2 orders of magnitude greater than that determined at 25 °C
- We are not in the position to derive stability constants yet:
 - Potential hydrolysis of $\text{ThO}_2 \rightarrow \text{Th}(\text{OH})_4^\circ$ in solid? pH slopes are identical:



Need to do XRD

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Preliminary Conclusions

- Considering that:
 - **Chloride** complexes were **not detected**
 - Speciation is **controlled by hydroxyl complexes**
- In acidic Cl-bearing natural hydrothermal solutions, behavior of Th likely has **different controls** compared to the REE

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Moving Forward

- Investigation of Th-sulfate (carbonate) speciation by similar experimental solubility method
- Synthesis of Th incorporated in solid phase (monazite) for further solubility experiments

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Acknowledgments



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